

# Intramolecular phase separation of copolymer "bottle brushes": No sharp phase transition but a tunable length scale

Hsiao-Ping Hsu, Wolfgang Paul, and Kurt Binder  
*Institut für Physik, Johannes Gutenberg-Universität Mainz*  
*D-55099 Mainz, Staudinger Weg 7, Germany*  
 (Dated: February 6, 2008)

A lattice model for a symmetrical copolymer "bottle brush" molecule, where two types (A,B) of flexible side chains are grafted with one chain end to a rigid backbone, is studied by a variant of the pruned-enriched Rosenbluth method (PERM), allowing for simultaneous growth of all side chains in the Monte Carlo sampling. Choosing repulsive binary interactions between unlike monomers and varying the solvent quality, it is found that phase separation into an *A*-rich part of the cylindrical molecule and a *B*-rich part can occur only locally. Long range order (in the direction of the backbone) does not occur, and hence the transition from the randomly mixed state of the bottle brush to the phase separated structure is strongly rounded, in contrast to corresponding mean field predictions. This lack of a phase transition can be understood from an analogy with spin models in one space dimension. We predict that the range of microphase separation along the bottle brush backbone can be controlled on the nanoscale by varying the solvent quality.

## I. INTRODUCTION AND MOTIVATION

Macromolecules with a comb-like architecture, where side chains are grafted to a linear (backbone) chain, find increasing interest: if the backbone is a rigid polymer, its solubility and processibility is improved [1, 2, 3]; if the grafting density of the side chains is very high, cylindrical "bottle brush"-shaped objects form, which under certain conditions show a thermally induced collapse transition to a spherical structure, providing interesting perspectives for the design of "molecular actuators" [4]; if copolymer bottle brushes are created by dense grafting of two types of side chains (*A*, *B*) on the backbone, interesting "horseshoe" and "meander"-like structures are observed, which is attributed to a local phase separation along the backbone of the bottle brush [5]. Clearly, this creates additional possibilities when one considers the desired [5] use of such shape persistent cylindrical macromolecules as building blocks in molecular assemblies. Thus, the problem of phase separation within a simple copolymer bottle brush has also found attention both by analytical theory [6] and computer simulation [7], the possibility to create "Janus cylinders" (upper half of the cylinder containing the *B* monomers, lower half containing the *A* monomers) was suggested, and predictions how the phase transition point from the randomly mixed state (where both *A* and *B* monomers are homogeneously distributed in the cylinder volume) to the separated state depends on the chain length of the side chains *N* were given [6].

In the case of flexible backbones there is a delicate interplay between the local segregation between the *A* and *B* side chains and the global geometric structure (such as "horseshoe", etc.) of the bottle brush, requiring a detailed and accurate understanding of the phase separation in these molecules. We reconsider this problem, performing Monte Carlo simulations of a similar model as in Ref. [7], but our analysis focuses on a different aspect, that has been completely ignored in the literature so far: single bottle brush molecules with side chains

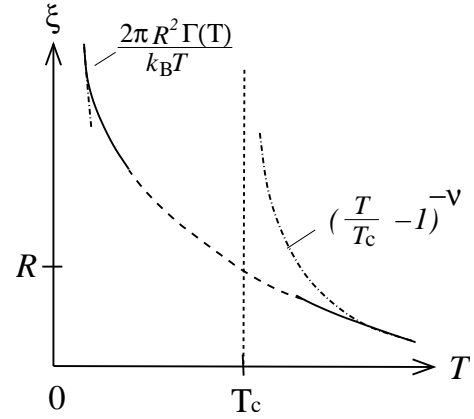


FIG. 1: Crossover scaling behavior of the correlation length  $\xi$  as a function of temperature  $T$ .  $\xi \propto (T/T_c - 1)^{-\nu}$  for  $T > T_c$ , and  $\xi \propto R^2 \Gamma(T)/k_B T$  for  $T < T_c$ .

of finite chain length *N* and very long, ideally infinitely long length of the backbone chain are quasi-one dimensional (1d) objects. Statistical mechanics of systems with short range interactions implies quite generally [8, 9] that there cannot be any sharp phase transitions in 1d systems in thermal equilibrium. A point in case is e.g. the 1d XY model, a chain of spins where each spin *i* is described by an angle  $\varphi_i$  in the *xy*-plane, with  $0 \leq \varphi_i \leq 2\pi$ . Neighboring spins along the chain experience a coupling  $-J \cos(\varphi_i - \varphi_j)$ . While mean field theories predict that ferromagnetic order along the chain occurs for temperatures  $T < T_c^{\text{MF}} = cJ$ , where *c* is a constant of order unity [8], an exact solution of this problem [8, 9] shows that ferromagnetic long range order is unstable against long-wavelength fluctuations, and actually the ferromagnetic correlation length  $\xi$  grows completely gradually as the temperature is lowered,

$$\xi = 2a(J/k_B T), \quad (1)$$

$a$  being the lattice spacing. Thus  $T_c = 0$ : note that  $\xi$  has to diverge when  $T_c$  is approached, and the singularity of  $\xi$  predicted by mean field theory at  $T = T_c^{MF}$  is completely washed out. This consideration can be generalized to cylinders of cross section area  $\pi R^2$  [10]. Then Eq. (1) gets replaced by a more complicated behavior that is sketched in Fig. 1. For  $T > T_c$  (the critical temperature of the corresponding bulk three-dimensional system)  $\xi \propto (T/T_c - 1)^{-\nu}$ , where  $\nu$  is the appropriate critical exponent, until  $\xi$  is of the order of  $R$ . Then the critical singularity is rounded off, and a crossover sets in to a relation analogous to Eq. (1)

$$\xi = 2\Gamma(T)\pi R^2/k_B T \propto (R^2/a)(J/k_B T), \quad T \rightarrow 0. \quad (2)$$

Note that the "spinwave stiffness" (helicity modules)  $\Gamma(T)$  characterizes the cost of long wavelength order parameter rotations, and  $\Gamma(T \rightarrow 0) \propto J$ . In the present work we shall provide evidence that the correlation length describing phase separation of a "Janus cylinder" type behaves qualitatively similar to Eqs. (1) and (2), cf. fig. 2b. Then the Flory-Huggins parameter  $\chi_{AB}$  that describes the incompatibility between  $A$  and  $B$  monomers takes the role that  $(J/k_B T)$  plays for the spin model. However, the problem whether for  $N \rightarrow \infty$  (and depending on the solvent condition) sharp phase transitions are restored is nontrivial, and in particular, describing the extent of rounding of the (mean field) transitions described in [6] by these long range fluctuations along the chain backbone remains a challenge.

## II. MODEL AND SIMULATION TECHNIQUE

As considered previously [6, 7], the generic model for this problem treats a completely rigid rod, oriented along the  $z$ -axis of a simple cubic lattice, and the side chains of type  $A$  and  $B$  are grafted in an alternating way, every site of the backbone chain being the grafting site of a side chain end. Of course, creating a statistical copolymer where the type of side chain along the backbone is chosen at random would be more realistic, from the experimental point of view. However, the quenched disorder thus introduced would encumber a theoretical treatment considerably, therefore this has not been considered previously [6, 7], and hence we study here regularly alternating copolymers, for the sake of better comparison to previous work. Also, we introduce a periodic boundary condition in  $z$ -direction, to avoid end effects associated with a finite backbone length.

The side chains are self-and mutually avoiding random walks. Between monomers of the side chains and monomers of the backbone chain only the excluded volume effect is considered. We allow for nearest neighbor interactions  $\epsilon_{AB}$ ,  $\epsilon_{AA} = \epsilon_{BB} = \epsilon$  between the respective pairs of monomers of the side chains, and hence the partition sum for this model is

$$Z = \sum q^{m_{AA}+m_{BB}} q_{AB}^{m_{AB}}, \quad (3)$$

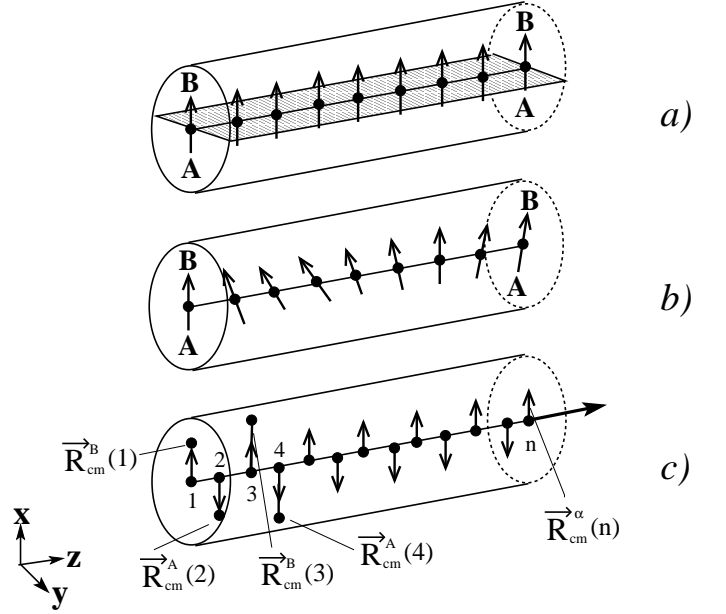


FIG. 2: Perfect phase separation of side chains in a binary ( $A, B$ ) copolymer bottle brush with alternating grafting sequence  $ABAB \dots$  into a "Janus cylinder" structure implies formation of an interface plane (part a), shaded) between the  $A$ -rich part (bottom) and the  $B$ -rich part (top) of the cylindrical bottle brush. The local orientation of this interface can be characterized by a vector oriented normal to it (arrows). At nonzero but low temperature phase separation will occur locally, but entropy will lead to long-wavelength fluctuations of the orientation of this vector (b), destroying axial long range order along the direction of the backbone of the bottle brush. Since the interface is not a sharp plane at nonzero temperature, but rather has a finite width, a numerical characterization of the local orientation of the interface is difficult. An essentially equivalent but numerically unambiguous characterization of this "Janus cylinder"-type ordering is achieved by calculating the unit vector from the grafting site ( $n$ ) of each chain to the projection of its center of mass position into the  $xy$ -plane  $\vec{R}_{cm}^\alpha(n)$ , see part (c).

where  $q = \exp(-\epsilon/k_B T)$ ,  $q_{AB} = \exp(-\epsilon_{AB}/k_B T)$ , and  $m_{AA}$ ,  $m_{BB}$ ,  $m_{AB}$  are the numbers of non-bonded occupied nearest neighbor monomer pairs  $AA$ ,  $BB$ , and  $AB$ , respectively. The sum in Eq. (3) extends over all possible configurations of these walks. Varying  $q$  in the range  $1 \leq q \leq 1.5$ , we cover the full range from good solvents ( $\epsilon = 0$ ) to poor solvents ( $\epsilon = 1.5$ ), since the  $\theta$ -solvent corresponds to a choice [11]  $q_\theta = \exp(-\epsilon/k_B T_\theta) \approx 1.3087$ . We vary  $q_{AB}$  in the range  $0 \leq q_{AB} \leq q$ : The case  $q_{AB} = 0$  corresponds to a very strong repulsion between  $A$  and  $B$ , while for  $q_{AB} = q$  the chemical incompatibility vanishes {recall that [12]  $\chi_{AB} \propto \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2$ }.

For our simulations, we use the pruned-enriched Rosenbluth model (PERM) [11]. This is a biased chain growth algorithm with population control. PERM has been applied very successfully both to linear and branched polymers (stars [13, 14], lattice animals [15]).

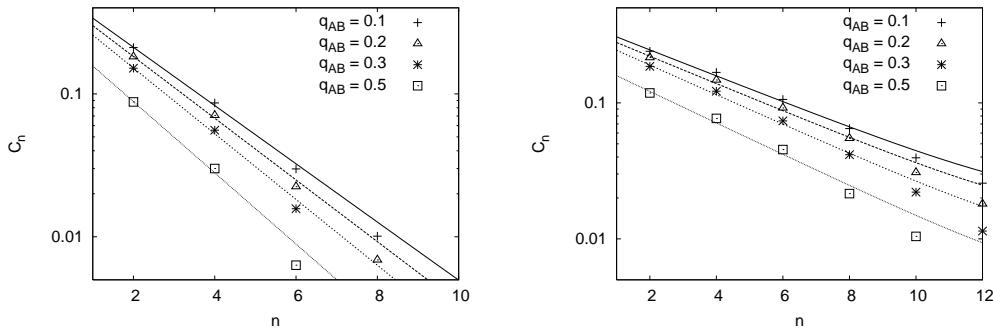


FIG. 3: Correlation function  $C_n$  describing the correlation of local phase separation along the backbone plotted vs. the distance  $n$  on a semi-log scale, for good solvent conditions ( $\epsilon = 0$ ),  $N = 6$  (left part) and  $N = 18$  (right part). All data are for  $L_b = 32$ , and several choices of  $q_{AB}$  are included, as indicated. Note that  $C_n \equiv (\langle \vec{S}_i^A \cdot \vec{S}_{i+n}^A \rangle + \langle \vec{S}_{i+1}^B \cdot \vec{S}_{i+1+n}^B \rangle)/2$ . Curves show the best fit to the data, i.e.  $C_n \sim [\exp(-n/\xi) + \exp(-(L_b - n)/\xi)]$

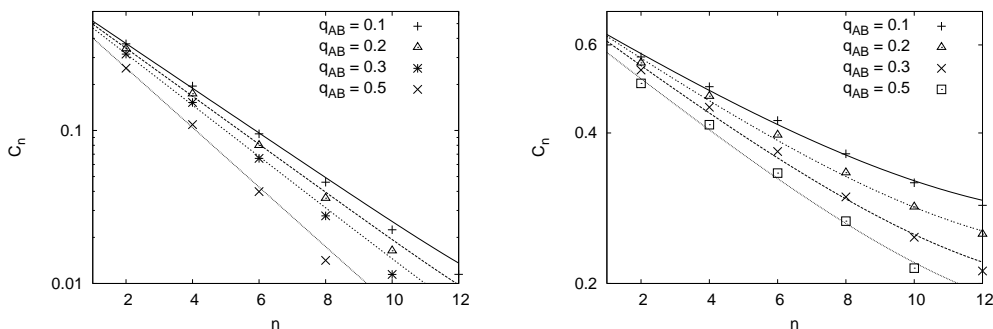


FIG. 4: Correlation function  $C_n$  plotted vs.  $n$  on a semi-log scale, for a poor solvent ( $q = 1.5$ ),  $L_b = 32$ ,  $N = 6$  (left) and  $N = 18$  (right). Several choices of  $q_{AB}$  are included, as indicated. Curves show the best fit to the data, i.e.  $C_n \sim [\exp(-n/\xi) + \exp(-(L_b - n)/\xi)]$

Similar to [13, 14], the bottle brush is generated by adding one monomer to each side chain until all side chains have the same number of monomers, thus growing all side chains simultaneously. For efficiency, side chains are grown with higher probabilities in the directions perpendicular to the backbone and in the direction where there are more free next neighbor sites. This additional bias must be taken into account by suitable weight factors. High statistics ( $10^5 \sim 10^6$  independent configurations) is obtained by using the population control (pruning/cloning) [11, 13, 14, 15]. The backbone length also is varied ( $L_b = 32, 48, 64$ ) to check that finite size effects caused by too small  $L_b$  are still negligible.

### III. RESULTS AND DISCUSSIONS

As has also been discussed in [7], the quantification of the phase separation that occurs in a bottle brush is difficult. We follow here an approach that is motivated by the

analogy with the spin problem mentioned in the introduction (fig. 2). We draw from each grafting site the vector  $\vec{R}_{cm}^\alpha$  to the center of mass (CM) of each side chain of type  $\alpha$  ( $\alpha = A$  or  $B$ ), and use the  $x$  and  $y$ -components of these vectors to define a unit vector  $\vec{S}_i^\alpha$  that points along that direction in the  $xy$ -plane. Making use of the fact that we have grafted  $A$  and  $B$  chains in an alternating way, we compute the correlation functions  $\langle \vec{S}_i^A \cdot \vec{S}_{i+n}^A \rangle$ ,  $\langle \vec{S}_{i+1}^B \cdot \vec{S}_{i+1+n}^B \rangle$ , for  $n = 0, 2, 4, 6, \dots$ . If we would have a symmetry breaking of "Janus cylinder" type (i.e. a plane containing the backbone exists, such that the  $A$ -monomers are on one side of this plane and the  $B$ -monomers on the other), the above correlations would not decay to zero as  $n$  increases, but rather settle down at a nonzero order parameter square. Figs. 3 and 4 show that this is not the case: for good solvent conditions  $q = 1$  even strong incompatibility ( $q_{AB} \rightarrow 0$ ) can induce only a correlation of rather short range. In poor solvents there is also little correlation when the side chains are very

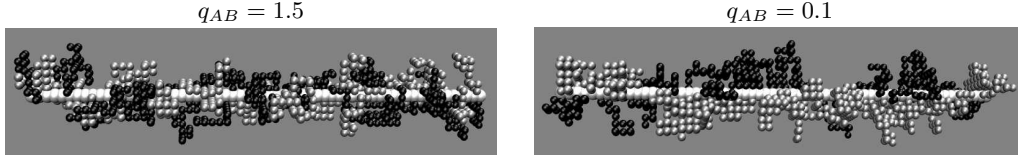


FIG. 5: Snapshots of the copolymer bottle brushes for a poor solvent ( $q = 1.5$ ),  $L_b = 64$ ,  $N = 18$ ,  $q_{AB} = 1.5$  (mixed state) and  $q_{AB} = 0.1$  (state with local phase separation). Monomers  $A$ , monomers  $B$ , and monomers on the backbone are shown in black, gray, and white colors, respectively.

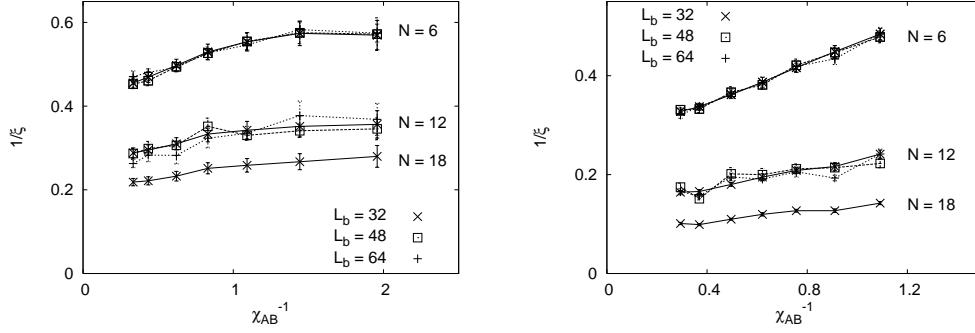


FIG. 6: Inverse of correlation lengths  $\xi$  vs.  $\chi_{AB}^{-1}$  for copolymer bottle brushes with backbone length  $L_b = 32, 48$ , and  $64$ , and three chain lengths  $N = 6, 12$ , and  $18$ . Both good (left) and poor (right) solvent conditions are shown.

short ( $N = 6$ ) and much stronger correlations occur for longer chains ( $N = 18$ ). Although our data are already somewhat affected by the finite length of the backbone (note the symmetry of  $C_n = C_{L_b-n}$ ), they are fitted by  $\exp(-n/\xi) + \exp(-(L_b - n)/\xi)$  quite well. In fig. 5 corresponding snapshots (similar to those of [7]) show rather pronounced phase separation, but this clearly is an artifact of the finite system size. The correlation lengths  $\xi$  which are determined by fitting  $C_n$  for  $n \geq 2$  as shown in fig. 3 and 4 are shown in fig. 6. As expected in view of the discussion given in the introduction,  $\xi$  increases gradually with increasing chemical incompatibility  $\chi_{AB}$  (decreasing temperature). Choosing poor solvent and/or  $N$  larger makes  $\xi$  also larger. Since  $1/\xi$  decreases linearly as  $\chi_{AB}^{-1} \rightarrow 0$ , one can extrapolate the data to  $\chi_{AB}^{-1} = 0$  by fitting a straight line  $1/\xi = 1/\xi_N + b/\chi_{AB}$ . Results of  $\xi_N$  in a poor solvent are shown in fig. 7. It gives an indication that a sharp phase transition ( $1/\xi_N \rightarrow 0$ ) will develop in the limit of large  $\chi_{AB}$  and large  $N$ . For very poor solvent condition, one expects that the brush fills a cylinder of radius proportional to  $\sqrt{N}$  densely, so the situation should be analogous to Eq. (2), with  $\pi R^2$  being replaced by  $N$ . Our data are roughly compatible with such an interpretation. However, the radial density profiles of the bottle brush molecules (fig. 7) show that the actual density profile  $\rho(r)$  is still far from a profile of a densely filled cylinder ( $\rho(r) = 1$  for  $0 < r < R$ ). This low density is probably responsible for the fact that  $\xi$  stays finite as  $\chi_{AB}^{-1} \rightarrow 0$  (fig. 6).

Alternatively, one could partition a bottle brush along

its backbone direction into disks with height  $a$  (distance between the neighboring grafting sites in our model). Each disk only contains one grafting site. The unit vector  $\vec{S}_i^\alpha$  is then defined by the direction from each grafting site to the CM of monomers of type  $\alpha$  ( $\alpha = A$  or  $B$ ) in the x-y plane. However, our results show that the correlation functions of this observable decay much faster due to the large fluctuations of the orientation of the vector  $\vec{S}_i^\alpha$ .

Summarizing these results, we have presented evidence that the phase separation towards a "Janus cylinder" structure develops completely gradually as the incompatibility between the two types of monomers increases. For our short side chain lengths, no trace of the sharp phase transitions predicted by Stepanyan et al. [6] could be detected (a similar conclusion was also reached in [7]). Very large length of side chains and/or very strong incompatibility is needed to produce a correlation extending over a large number of side chains. The fluctuation that has been ignored by the mean field theory [6], long wave length random "twist"-like rotation of the local interface between the  $A$ -rich and  $B$ -rich region in the "Janus cylinder", costs very little energy and destroys long range order dramatically (fig. 2b). On the other hand, varying suitably side chain length and solvent quality one can control the nanoscopic length scale over which Janus-type phase separation occurs along the backbone of the bottle brush. For asymmetric side chain lengths (and flexible backbones) this length scale is related to the spontaneous curvature of the cylinder-shaped bottle brush polymer.

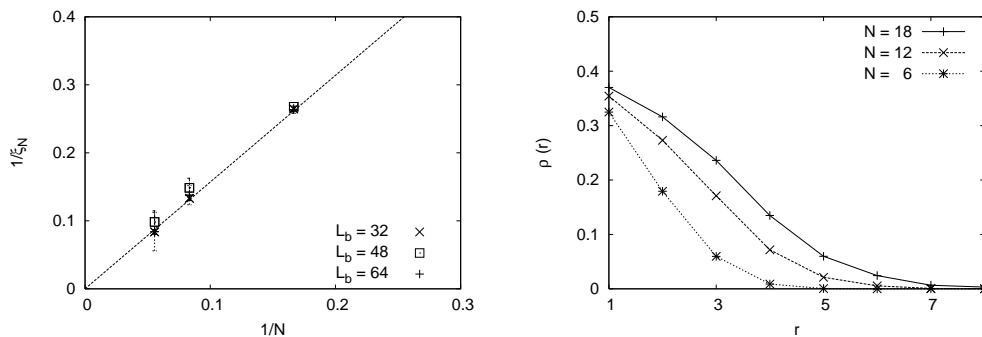


FIG. 7: Inverse of correlation length  $\xi_N$  in the limit of  $\chi_{AB} \rightarrow \infty$  vs.  $1/N$  for a poor solvent ( $q = 1.5$ ). The straight line shows the asymptotic behavior as  $N \rightarrow \infty$  (left part). Monomer density profile  $\rho(r)$  plotted vs.  $r$  for a poor solvent ( $q = 1.5$ ),  $q_{AB} = 0.1$  and  $L_b = 64$  (right part).

Controlling this curvature is desirable for the anticipated application of such molecules in nanotechnology [5].

#### IV. ACKNOWLEDGMENTS

H.-P. H. thanks Prof. Peter Grassberger and Dr. Walter Nadler for very useful discussions. K. B. thanks M.

Schmidt for stimulating discussions. This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG), SFB 625/A3.

- 
- [1] Ciferri A., Krigbaum W. , and Meyer R. "*Polymer Liquid Crystals*", Academic press, New York, (1982).
  - [2] Wegner G. Mol. Cryst. Liq. Cryst. Sci. Technol. A **216** (1992) 7.
  - [3] Cao Y., and Smith P. Polymer **34** (1993) 3139.
  - [4] Li C., Gunari N., Fischer K., Jansonff A., and Schmidt M. Angew. Chem. Int. Ed. **43** (2004) 1101.
  - [5] Stephan T., Muth S., and Schmidt M. Macromolecules **35** (2002) 9857.
  - [6] Stepanyan R., Subbotin A., and ten Brinke G. Macromolecules **35** (2002) 5640.
  - [7] de Jong J., and ten Brinke G. Macromol. Theory Simul. **13** (2004) 318.
  - [8] Domb C., and Green M. S. "*Phase transitions and critical phenomena*", Vol.1, Academic press, New York, (1971).
  - [9] Baxter R. J. "*Exactly solved models in statistical Mechanics*" Academic Press, New York, (1982).
  - [10] Fisher M. E. and Privman V. Phys. Rev. B **32** (1975) 477; Pichard J. L. and Sarma, G. J. Phys. C **14** (1981) L617.
  - [11] Grassberger P. Phys. Rev. E **56** (1997) 3682.
  - [12] Flory P. J. "*Principles of polymer chemistry*" Cornell University Press, Ithaca, (1953).
  - [13] Hsu H.-P., Nadler W., and Grassberger P. Macromolecules **37** (2004) 4658.
  - [14] Hsu H.-P. and Grassberger P. Europhysics Lett. **66** (2004) 874.
  - [15] Hsu H.-P., Nadler W., and Grassberger P. J. Phys. A: Math. Gen. **38** 2005 775.